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NBS TECHNICAL NOTE 1154

U.S. DEPARTMENT OF COMMERCE / National Bureau of Standards

A Programmable Sample Dryer for Thermal Ionization Mass Spectrometry

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A Programmable Sample Dryer for Thermal Ionization Mass Spectrometry

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A PROGRAMMABLE SAMPLE DRYER FOR THERMAL IONIZATION MASS SPECTROMETRY

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A sample dryer has been designed which allows reproducible and automatic filament current and timing adjustments for up to five separate steps. Designed around inexpensive TTL logic, the dryer may be programmed by resistors on a plug-in card to provide the proper drying conditions, be programmed to stop and signal the operator after any step, or be allowed to continue uninterrupted through the entire drying sequence. A programmable 110 volt output is provided for controlling a heat lamp or other accessory.

Key words: isotopic analysis; isotopic fractionation; sample dryer; thermal ionization mass spectrometry.

1. Introduction

Samples for isotope ratio measurements by thermal ionization mass spectrometry are usually dried on a filament from a solution of a soluble salt before insertion into the mass spectrometer. Frequently, the drying procedure entails a sequence of drying times and temperatures. As in the case of the analysis of lead, zinc, and cadmium by the silica gel method [1,2], it may be necessary to add additional reagents to the filament at preset intervals during the drying procedure.

The process of thermally ionizing an element from a hot filament causes a mass dependent fractionation of the isotopic ratios. The rate and magnitude of the isotopic fractionation is dependent, at least in part, upon the chemical species present on the filament, and in the case of a multiple filament ion source, the molecular species resulting from vaporization of the sample from the filament. The theoretical and empirical aspects of the isotopic fractionation problem have been covered in some detail by Moore et al., [3]. The chemical species formed by drying a sample on a filament can be quite complex. For example, it has been shown that calcium nitrate, in a dilute nitric acid solution, produces a mixture of calcium rhenates when dried on a rhenium filament [3]. These species include Ca_2ReO_4, $Ca_3Re_2O_9$, $Ca_6Re_2O_{11}$, and $Ca_5Re_2O_{12}$.

Obtaining precise and accurate mass spectrometric isotope ratio measurements requires that all samples (standards and unknowns) show the same rate and degree of isotopic fractionation during the analysis. Only if this condition is met, can unknown samples be compared with the standards and corrected to absolute isotopic ratios, in those cases where standards of known absolute isotopic composition are available. This condition of comparable isotopic

fractionation can be met only if the standards and unknowns are in the same chemical form on the filament.

It has been generally accepted for some time that variations in the drying procedure between sample loadings can decrease the accuracy of mass spectrometric isotope ratio measurements, and most laboratories engaged in this type of analysis make some attempt to reproduce the sample loading procedure. However, the magnitude of the errors that can result from sample loading variations is not fully appreciated. Uranium isotopic ratios, for example, can be shifted by as much as 0.25 percent by small filament temperature differences during the sample loading. Errors of this magnitude are unacceptable for use in the accountability and safeguarding of nuclear materials. Recent work in this laboratory [4,5] has indicated that "state-of-the-art" isotope ratio measurements (i.e., 0.01 percent or less uncertainty) for some elements require extremely close tolerances on sample drying parameters. Such reproducibility is difficult, if not impossible, to achieve manually.

The potential for errors attributable to sample loading variations is especially great in high volume laboratories where several analysts, often working in shifts, may each analyze parts of a suite of samples. The inter-analyst data may show systematic biases, in addition to the random and intra-analyst variations. Automated sample drying can substantially reduce these systematic biases, as well as minimize the variations inherent in manual control of current settings and drying times.

The sample dryer, described herein, has been in operation on a daily basis in the mass spectrometry laboratory, Inorganic Analytical Research Division, for the past 4 years. Five such units are currently in operation and have proven to be extremely trouble free and reproducible. They have contributed, not only to improved accuracy and precision, but also to increased sample analysis output.

2. Electronic Circuit Operation

The electronic circuitry is comprised of a digital programming section (figure 1) and an analogue constant filament power supply (figure 2). The digital programmer selects the proper current circuit, as well as the duration of the time interval for each current selected.

The digital programmer is made up of a single BCD counter (U6) with its output state indicated by a seven segment LED. The output is also decoded by a one-of-ten decoder (U5) which selects one of the five timed, current active states or one of the four halt states. Programming is accomplished by means of a personality card (22 pin PC card, figure 3) with jumpers, timing resistors, and current control resistors selected, to provide parameters tailored to the particular element being dried on the sample filament. The state selected is routed by the personality card to produce the desired functions. A halt state can be jumpered to allow continuation to the next current active state, or when left open, sound an alarm and interrupt the filament current. Resumption of operation, at the next current active state, occurs when the operator presses the start-continue button. When a current active state is selected, one resistor is used to establish the filament

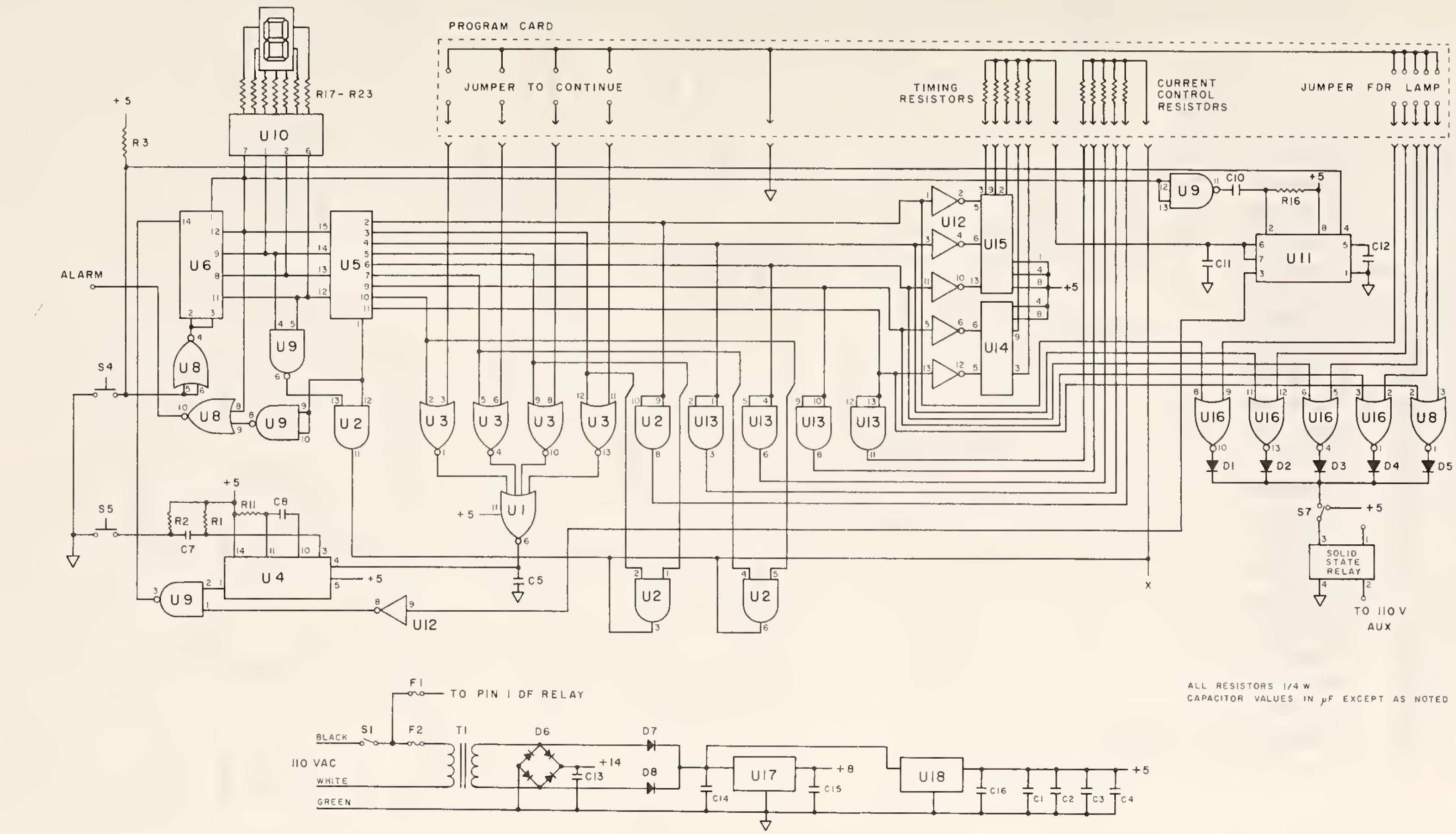


Figure 1. Digital programming section schematic.

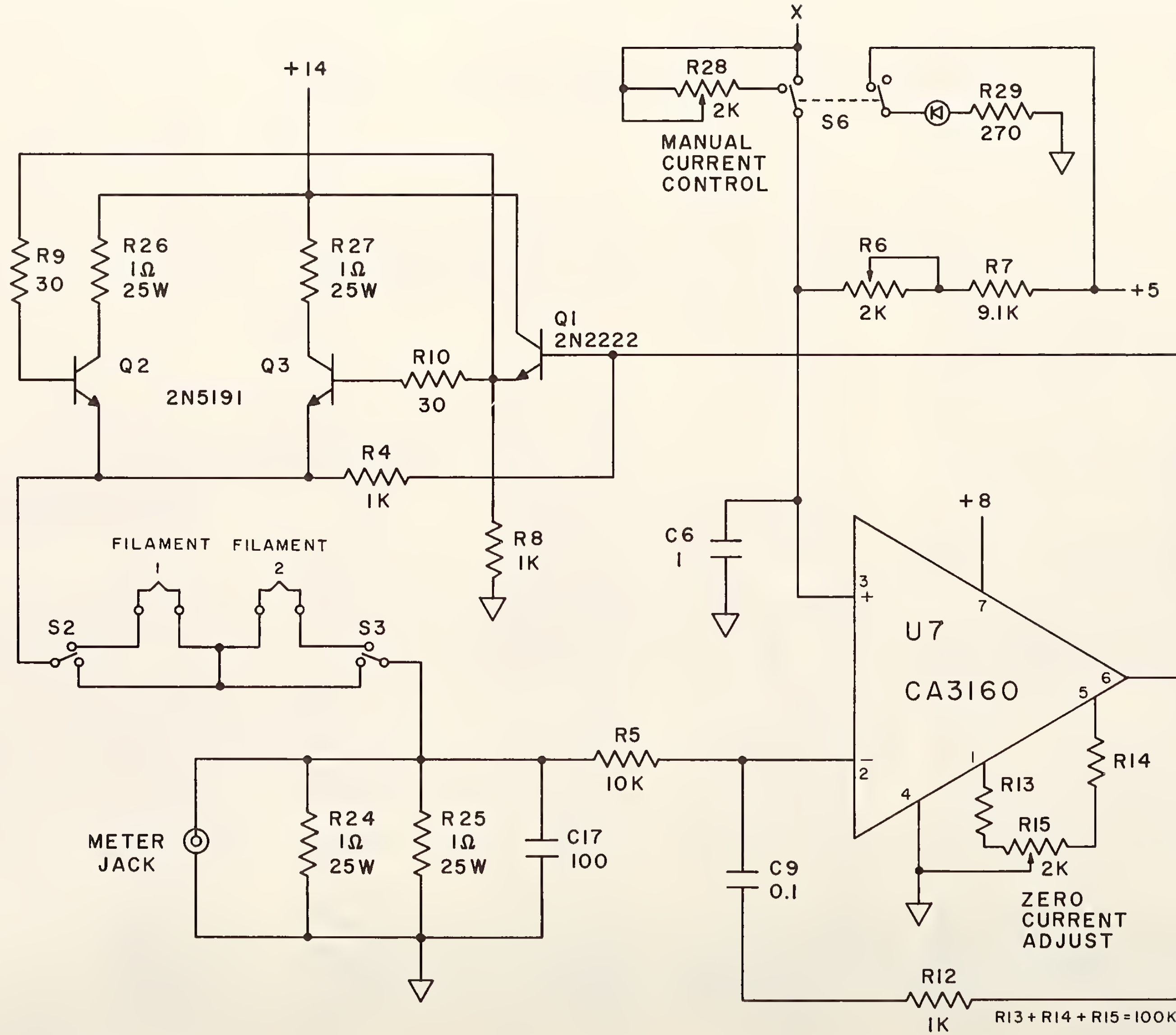


Figure 2. Analogue constant current section schematic.

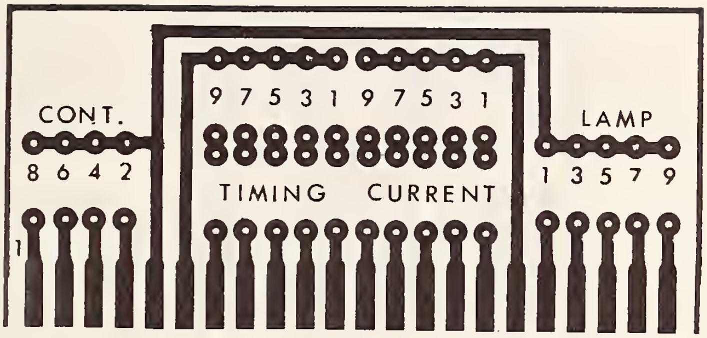


Figure 3. Personality Card PC layout.

current, while another resistor determines the time interval. The timing resistors are individually connected to a +5 V source through an analogue switch (U15, U16) to become the pull-up resistor of the 555 one-shot circuit (U11). The output of the one shot returns to the state counter, advancing the state at the one-shot's time out. During the time interval defined for a given state, the filament current is set by the current control resistor selected. Each current control resistor is connected as one element of a voltage divider and is selected by means of one of five open collector TTL gates (U13, U2) when the selected output goes active low. The voltage level established determines the filament set current.

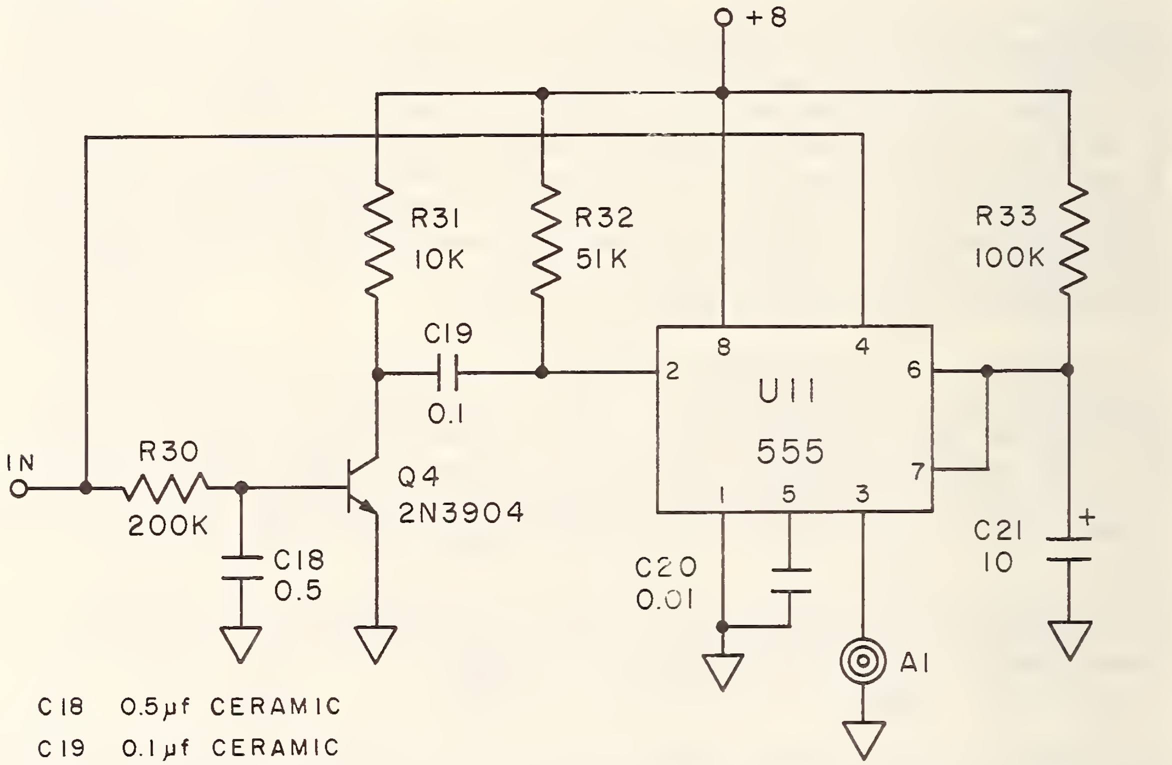
Halt states are provided between each active state and are bypassed by appropriate jumpers. When the halt state is entered, the signal is logically enabled by the presence of a jumper through one of the four gates (U3). The output is collected through an or-gate (U1) and used to trigger the start-continue one shot (U4), which immediately advances the state counter. This one shot is also activated by the start-continue push button.

The final aspect of the digital circuitry provides an auxiliary 110-Vac output activated at any active state desired and selected by a jumper. One or more jumpers enable the gates (U8, U16), which operate the solid state relay when the selected state signal is present.

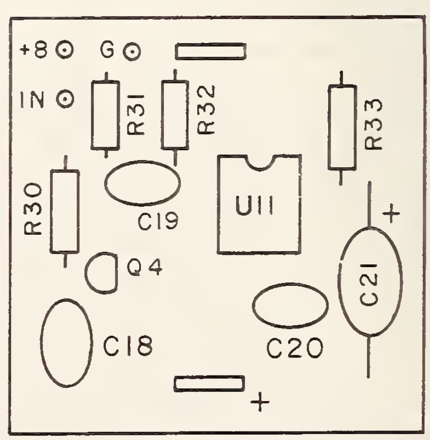
The analogue section of this device supplies a programmed constant current to the filament being dried. The current that is supplied is proportional to the voltage determined by the resistor on the personality card. This voltage is applied to the non-inverting input of the operational amplifier (U7). The output of the operational amplifier drives transistor Q1, whose output, in turn, drives transistors Q2 and Q3 as a double emitter follower or "Darlington circuit". The emitter outputs of Q2 and Q3 supply current to the filament which is connected to ground through the current metering resistors R24 and R25. The voltage developed across the metering resistors is returned to the inverting input of the operational amplifier to complete the negative feedback loop. In this configuration, the operational amplifier maintains its output voltage at the level necessary to drive the output transistors to source a current through the sample filament and metering resistors, providing a feedback voltage developed across the metering resistors that exactly matches the programmed input voltage. Components R12, R5, and C9 are used to insure stability of the circuit under various load and voltage conditions.

Power is supplied to this system by a transformer input and diode bridge rectifier circuit. Unregulated power is used for the filament source current. A regulated +5 volt source (U18) supplies power to the TTL logic, and a regulated +8 volts (U17) is used to drive the operational amplifier.

The alarm signal output from the main circuit board provides a continuous high output from the U8 gate. This can be fed into an alarm circuit (figure 4) to provide a one shot signal of a fixed duration. The length of the audible signal can be adjusted by varying the value of R33 or C21. The RC time constant of R30 and C18 is sufficient to prevent triggering of the 555 one shot (U11) when the unit advances automatically to the next active state. The alarm circuit board (figure 5) is designed to mount directly on the terminals of the signal device.



C18 0.5µf CERAMIC
C19 0.1µf CERAMIC
C20 0.01µf CERAMIC
C21 10µf ELECTROLYTIC
R30 200 K
R31 10 K
R32 51 K
R33 100 K
Q4 2N3904
U11 555 TIMER
A1 ELECTRONIC SIGNAL DEVICE, 2900 Hz



ALL RESISTORS 1/4W TIN OXIDE

Figure 4. Schematic, layout, and parts list for alarm.

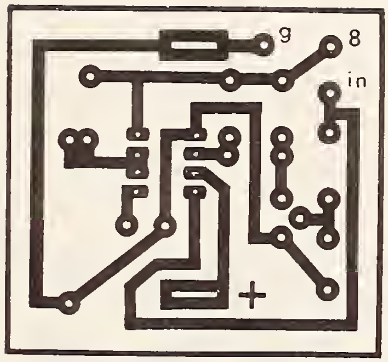


Figure 5. PC board for alarm.

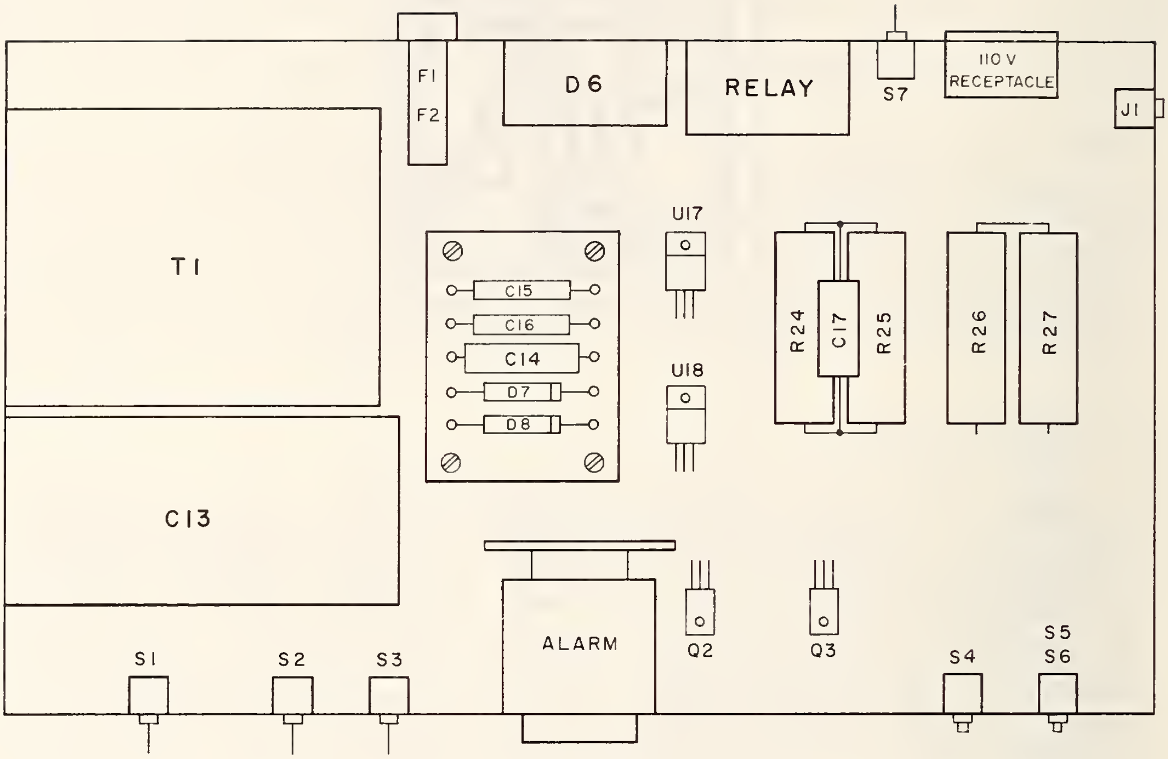
3. Construction

The sample dryer can be contained in an inverted 12" x 7" x 3" aluminum chassis box. The power supplies, controls, and high current components are mounted on the chassis box (figure 6), while the remainder of the circuitry is mounted on the main PC board (figures 7, and 8). The component layout for the main circuit board is given in figure 9. The main circuit board is mounted on the side and near the top of the chassis, and is attached by means of a 22-contact edge card receptacle soldered to the board. Connections between the main circuit board and the chassis-mounted components are provided through a 16-pin DIP socket, allowing for easy removal of the board. Ground and +5 volt supply voltage to the TTL logic are provided through screw terminals on the board. The manual current control (R28), filament sockets, and heat lamp assembly are attached to a 12" x 7" x 1/8" aluminum plate mounted on the chassis with 1/2" standoffs. Figure 10 shows the positioning of these components. The standoffs provide for air circulation under the plate to minimize the heating of the electronics by the lamp. The chassis-mounted phone jack allows monitoring of the voltage across R24-R25, which is numerically equal to one-half of the current through the filaments. Switch S7, mounted on the back of the chassis, allows operation of the 110-Vac auxiliary output without entering one of the current active states.

4. Calibration and Operation

Offset voltage nulling of the operational amplifier (U7) is accomplished with a 100 KΩ variable resistance (R13-R15), connected across terminals 1 and 5, with the potentiometer slider arm connected to ground. The offset voltage should be set to produce zero current at the filament when the dryer is in a halt state.

If more than one sample dryer is in operation in a laboratory, it may be desirable to have interchangeability of the personality cards among the units. Potentiometer R6 can be used to adjust the voltage divider output to the noninverting input of the operational amplifier to compensate for small differences in the output voltage of the +5 volt regulators (U18) in the different units. Through adjustment of R6, the five sample dryers in this laboratory produce the same current (over the range of 0-2 A) to within 0.2



ACTIVE COMPONENTS	
U17	7808
U18	7805
Q2, Q3	2N5191
D6	10A BRIDGE RECTIFIER
D7, D8	1N 4001
RELAY	PHOTO ISOLATED SOLID STATE RELAY, 110 VAC 10 A 3-32 VDC CONTROL SIGNAL

PASSIVE COMPONENTS	
C13	14000μF ELECTROLYTIC
C14	2000μF ELECTROLYTIC
C15, C16	0.5 μF
C17	100 μF
R24-R27	1Ω 25W
S1-S3, S6	DPDT 5A MIN. TOGGLE
S7	SPDT 5A MIN. TOGGLE
S4, S5	SPST PUSHBUTTON, N.O.
T1	TRANSFORMER, 10V 8A
J1	MIN. PHONE JACK, N.O.
F1	2.5A SLO-BLO FUSE
F2	1A FUSE
110V REC.	3 WIRE FEMALE POWER LINE CONNECTOR

Figure 6. Chassis layout and parts list.

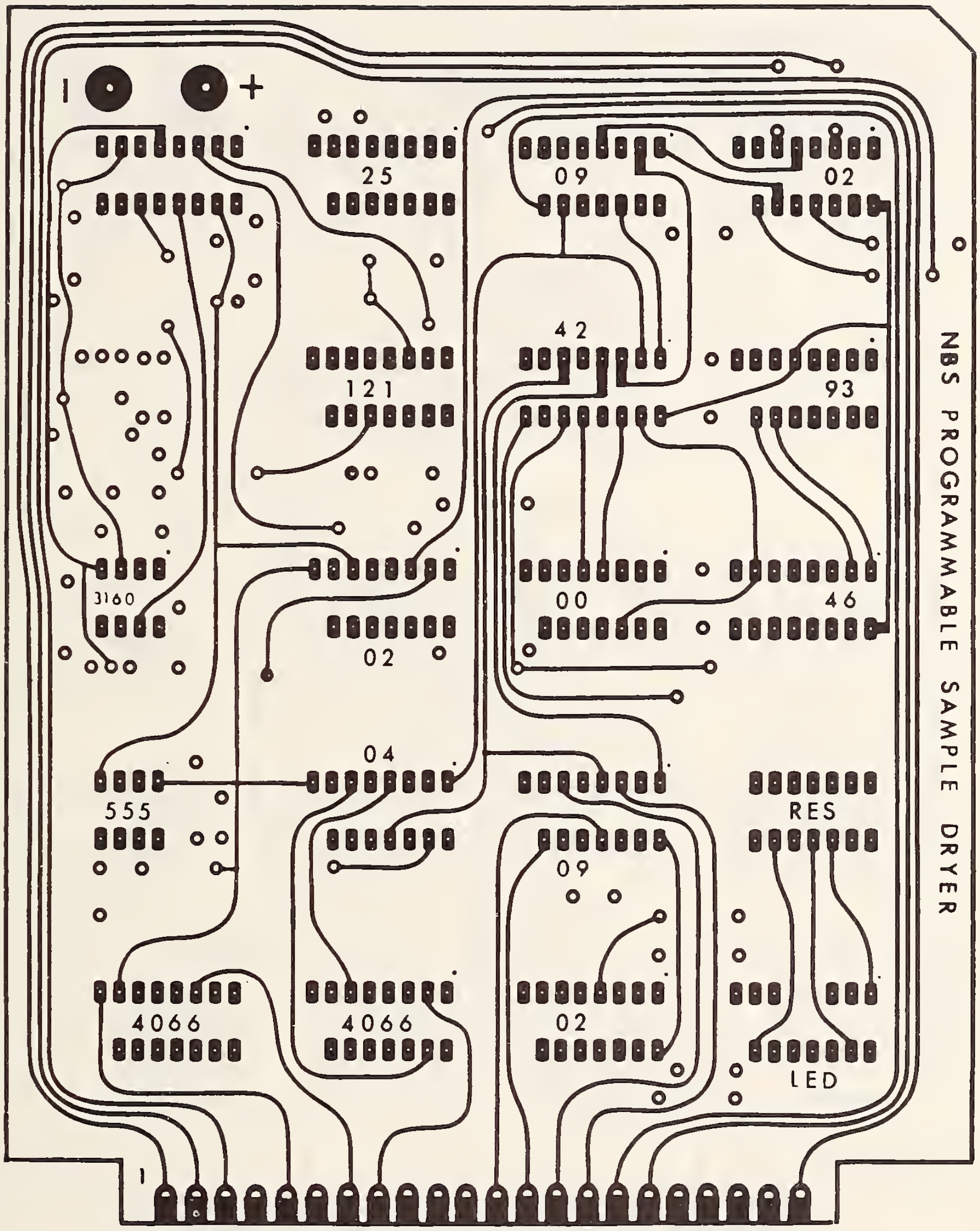


Figure 7. Main PC board (front).

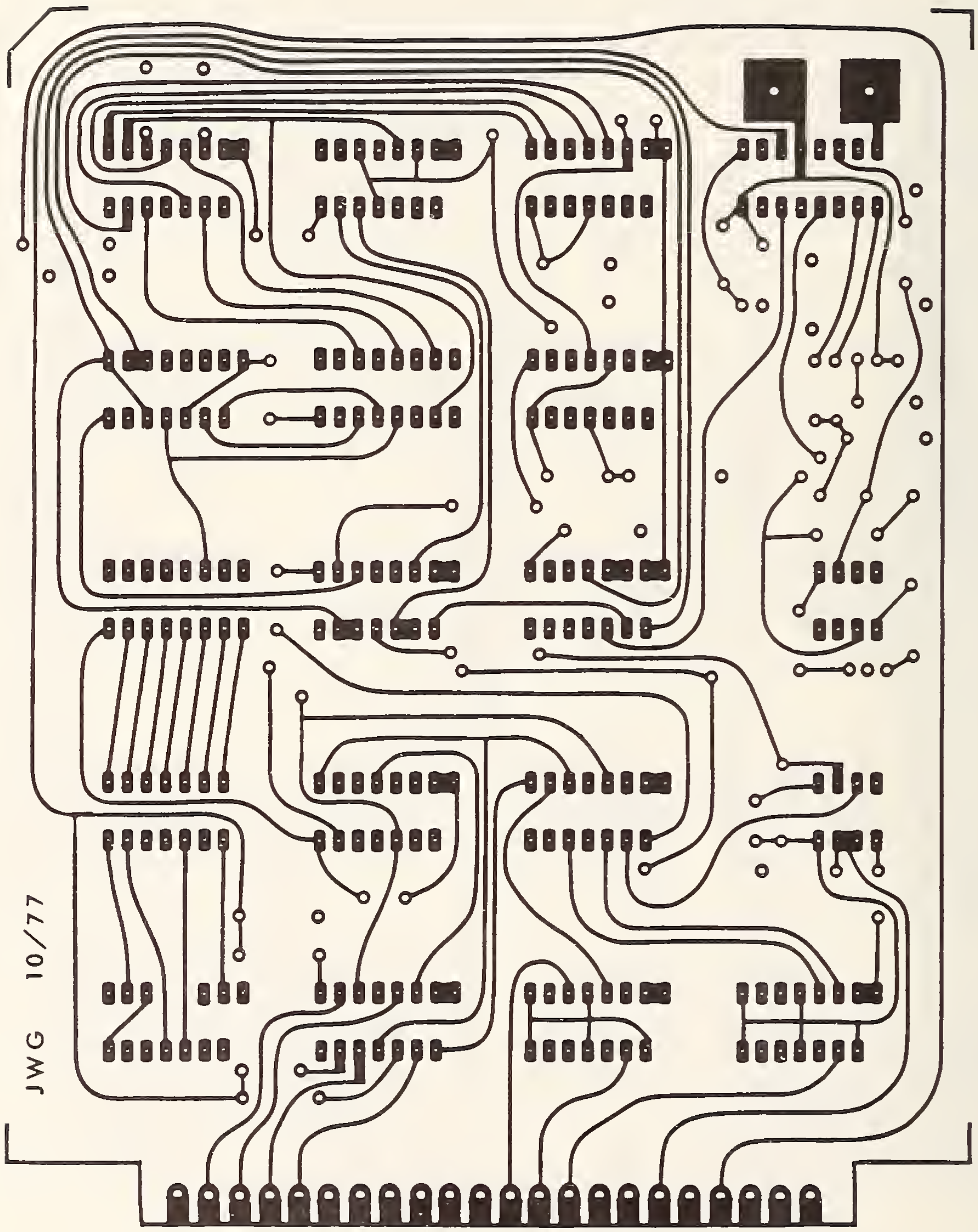
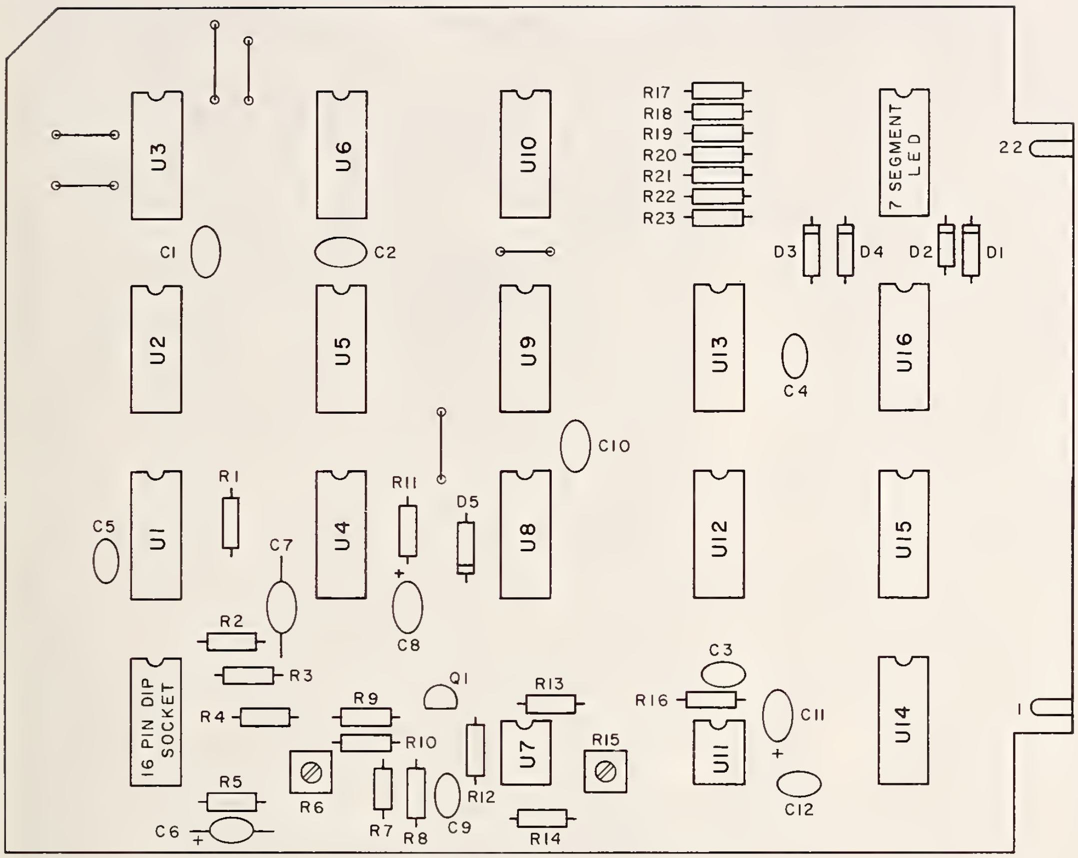


Figure 8. Main PC board (back).



ACTIVE COMPONENTS

U1	7425
U2, U13	7409
U3, U8, U16	7402
U4	74121
U5	7442
U6	7493
U7	CA3160
U9	7400
U10	7447
U11	555
U12	7447
U14, U15	CD4066
D1 - D5	1N270
Q1	2N2222

PASSIVE COMPONENTS

C1 - C4, C9	0.1 μF CERAMIC
C5	50 pF CERAMIC
C6, C8	1 μF TANTALUM
C7	0.05 μF
C10	1000 pF SILVER MICA
C11	100 μF TANTALUM
C12	0.01 μF CERAMIC
R1, R3, R5, R16	10 K
R2	500 K
R4, R8, R12	1 K
R6, R15	2 K SINGLE TURN
R7	9.1 K
R9, R10	30
R11	39 K
R13 + R14	98 K TOTAL
R17 - R23	270

ALL RESISTORS 1/4 W TIN OXIDE

Figure 9. Main circuit board layout and parts list.

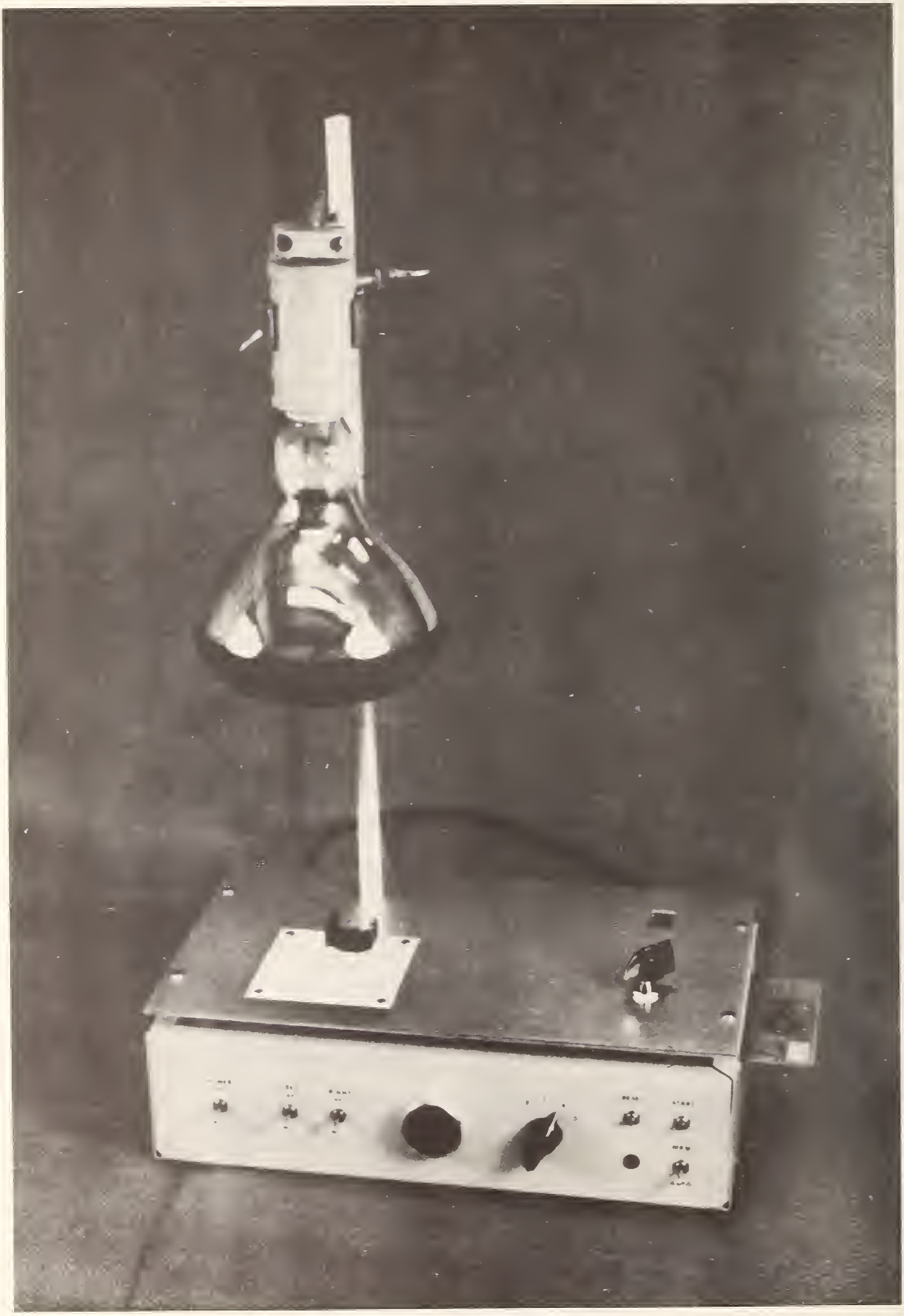


Figure 10. Sample dryer.

percent from the same personality card. For multiple units, it is also necessary to match the timing capacitor (C11) of the 555 one shot to achieve personality card interchangeability.

The relationship between the values of the timing resistors and the time of the current active states is given in figure 11. The similar relationship between the values of the current control resistors and the filament currents is given in figure 12. For the most accurate settings, the dryer should be calibrated with resistors of known value, rather than relying on figures 11 and 12.

Although the 110-Vac programmable output is most frequently used to control a heat lamp used to aid the drying process, it can also be used to control external temperature sensing instrumentation. One unit in this laboratory is interfaced to a digital remote sensing infrared thermometer, capable of monitoring the filament temperature in the range of 400 °C to 1650 °C. For filament drying temperatures above 400 °C, the programmed 110-Vac output allows the infrared thermometer to control the filament current by means of an output control signal, proportional to the difference between the filament temperature and a preset temperature. Timing of the high temperature drying is still controlled by the personality card timing resistor for the particular current active state.

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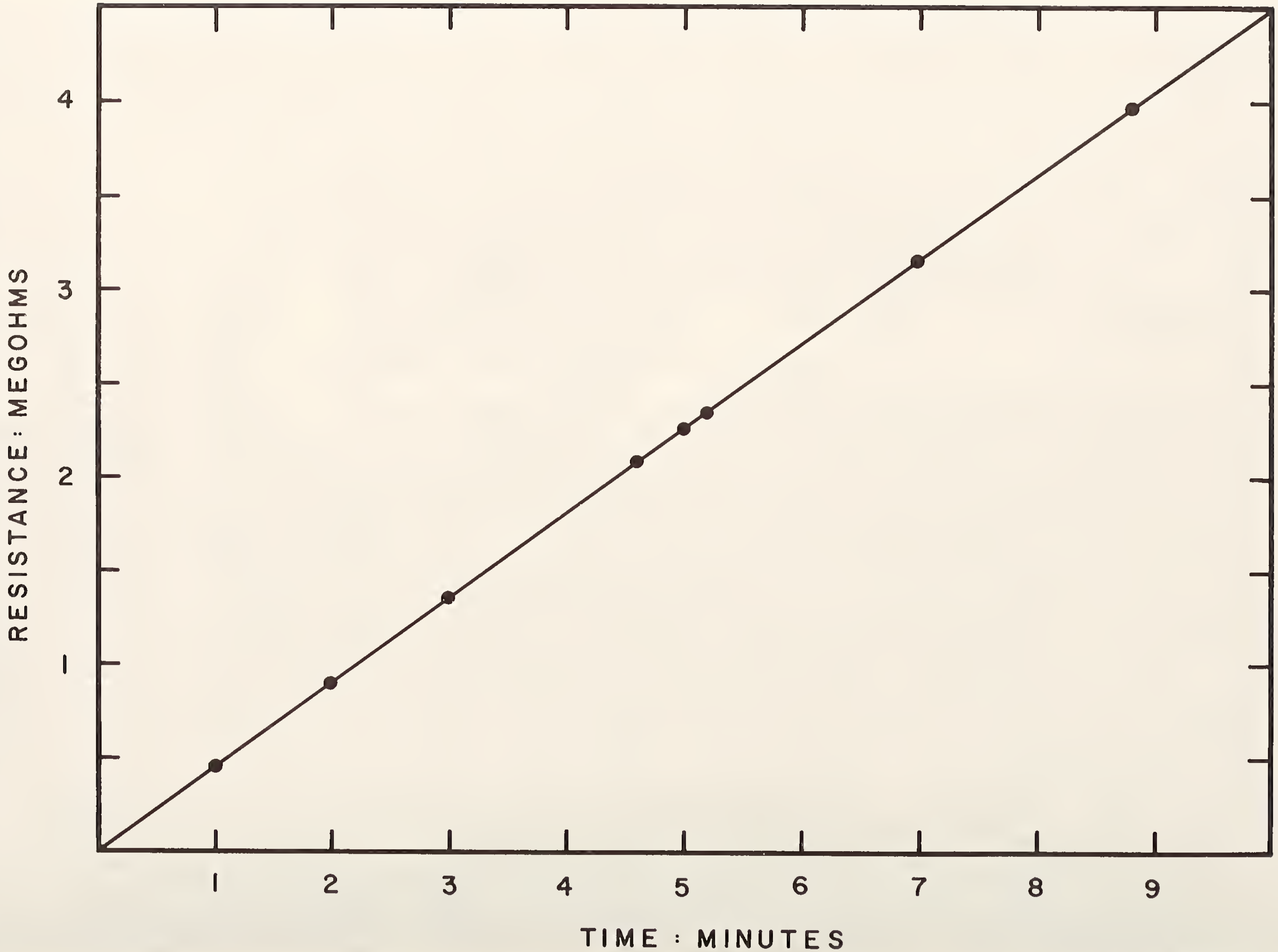

Figure 11. Time *vs*. resistance calibration plot.

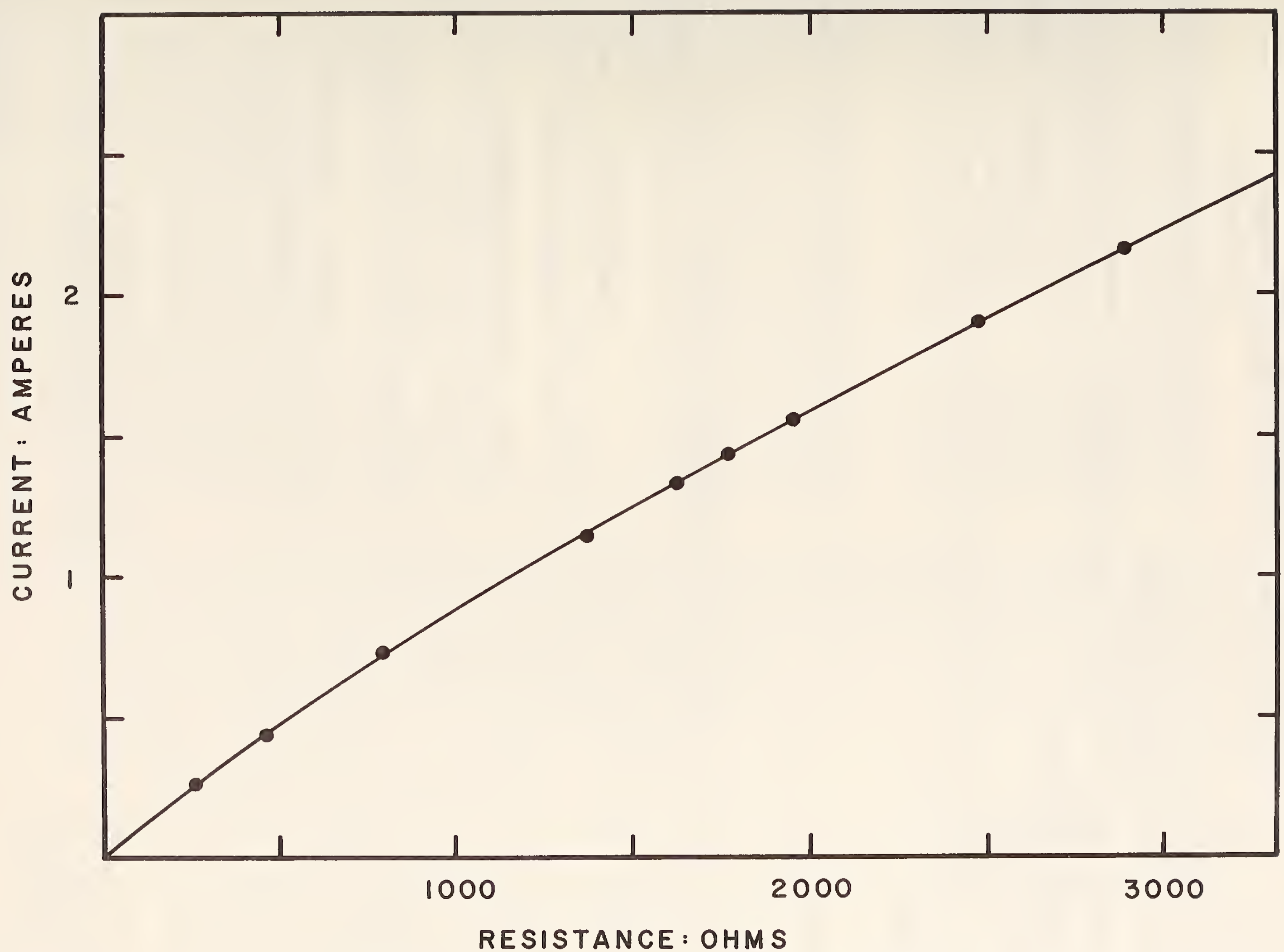

Figure 12. Current vs. resistance calibration plot.

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7. Contract/Grant No.

8. Type of Report & Period Covered

Final

9. SPONSORING ORGANIZATION NAME AND COMPLETE ADDRESS (Street, City, State, ZIP)

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10. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

11. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)

A sample dryer has been designed which allows reproducible and automatic filament current and timing adjustments for up to five separate steps. Designed around inexpensive TTL logic, the dryer may be programmed by resistors on a plug-in card to provide the proper drying conditions, be programmed to stop and signal the operator after any step, or be allowed to continue uninterrupted through the entire drying sequence. A programmable 110 volt output is provided for controlling a heat lamp or other accessory.

12. KEY WORDS (Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)

isotopic analysis; isotopic fractionation; sample dryer; thermal ionization mass spectrometry.

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